

PATENT SPECIFICATION

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(54) METHOD OF SILYLATING ORGANIC VINYLIC POLYMERS

(71) We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to making organic vinylic polymers having functional organosilyl groups thereon.

The introduction of silicon functional groups into organic vinylic polymers is desirable to add versatility to the usefulness of organic vinylic polymers. The use of hydrolysable functional silicon groups introduces the ability of the organic vinylic polymer to be cross-linked at room temperature. Thus, an object of the present invention is to provide a method for introducing organosilyl groups into organic vinylic polymers.

Accordingly the present invention provides a method of preparing silyl-terminated organic vinylic polymers which comprises polymerising organic vinylic monomers by means of free radical initiation in the presence of an organosilicon compound of the formula



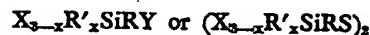
in which R' is a monovalent hydrocarbon radical free of aliphatic unsaturation and having from 1 to 18 carbon atoms, R is a divalent hydrocarbon radical free of aliphatic unsaturation and having from 1 to 18 carbon atoms, X is a monovalent hydrolysable radical as hereinafter defined, x is 0, 1 or 2 and Y is a free radical activated group having a chain transfer constant greater than 10^{-3} .

The polymerisation of organic vinylic monomers by means of free radical initiators is well known in the art. For example, the organic vinylic monomers can be polymerised by the free radical initiation employing a

peroxide, such as an organic peroxide, ultra-violet light, triphenylmethane, diazonium compounds, persulphates, aliphatic azobisnitriles, heat or high energy radiation. These polymerisation processes are well known in the art, and accordingly no detailed description is provided herein. The polymerisations can be carried out by bulk polymerisation, organic solvent polymerisation, emulsion polymerisation or suspension polymerisation. However, the particular polymerisation technique should take into consideration the hydrolysable groups bonded to the silicon atom. Where aqueous systems are to be used the absence of catalytic agents for the hydrolysis of the hydrolysable groups should be avoided. The particular hydrolysable group should also be considered. For example, alkoxysilicon compounds are less susceptible to hydrolysis in the absence of a catalyst than most other hydrolysable groups on silicon. Thereafter, in aqueous emulsion and dispersion polymerisations X is preferably alkoxy. However, there is no need to exclude other hydrolysable groups from polymerisations using water, if there is no desire to retain the hydrolysable groups in the unreacted state in the resulting polymerised product.

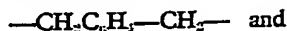
The method of polymerising the organic vinylic monomers by means of free radical initiation is modified to the extent that there is present during the polymerisation an organosilicon compound of a defined class which has a chain transfer constant greater than 10^{-3} . The presence of this particular organosilicon compound during the free radical polymerisation of the organic vinylic monomers results in organic vinylic polymers having silicon functional terminating groups.

The particular class of organosilicon compounds having a chain transfer constant of greater than 10^{-3} and suitable for the present invention have a formula



[Price 25p]

where R', R, X, z and Y are as above defined. Examples of R' include methyl, ethyl, propyl, isopropyl, butyl, phenyl, octyl, octadecyl, benzyl, naphthyl, xenyl, cyclopentyl, cyclohexyl, methylcyclohexyl, tolyl, xylyl, 4-isopropylphenyl and 2-phenylpropyl groups. Examples of R include methylene, ethylene, propylene, butylene, hexylene, octadecylene, phenylene, tolylene, xylene, xenylene, naphthylene, cyclohexylene,



groups.

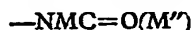
X can be any hydrolysable group such as a halogen atom; a group of the formula —OZ when Z is any hydrocarbon or halogenated hydrocarbon group of from 1 to 18 carbon atoms, any hydrocarbon ether radical, any acyl radical, or any N,N-amino radical. X can also be any amino radical, any ketoxime radical of the formula



in which M is any monovalent hydrocarbon or halogenated hydrocarbon radical Z, and M' is any divalent hydrocarbon radical both valences of which are attached to the carbon all ureido groups of the formula



in which M is defined above and M'' is H or any of the M radicals; a carbamate group of the formula —OOCNMM'' in which M and M'' are defined above, or a carboxylic amide radical of the formula



in which M and M'' are defined above. X can also be a sulphate group or sulphate ester group of the formula —OSO₂(OM) where M is defined above; a cyano group; an isocyanate group; or a phosphate group or phosphate ester group of the formula



in which M is defined above.

The term "hydrolysable group" means any group attached to the silicon which is readily hydrolysed by water at room temperature.

Y includes any of the groups which are activated by free radical initiators and have a chain transfer constant greater than 10⁻³. For example, Y can be a bromine atom, a

mercapto or an amino group. The determination of chain transfer constants is well known in polymer chemistry and the organosilicon compounds of the present invention have chain transfer constants similar to organic compounds of the formula HRY.

The polymerisable or copolymerisable organic vinylic monomers include the styrene class, such as styrene, alpha-methylstyrene, vinyltoluene, 4-bromostyrene, 4-chloro-3-fluorostyrene, 2-chlorostyrene, 2,5-dichlorostyrene, 2,5-difluorostyrene, 2,4-dimethylstyrene, 4-ethoxystyrene, 4-hexyldecylstyrene, 3-hydroxymethylstyrene, 4-iodostyrene, 4-isopentoxystyrene or 4-nonadecylstyrene. Other vinyl group containing organic monomers include ethylene, propylene, cyclohexene, divinylbenzene, indene, hexadecene, tetrafluoroethylene, vinylchloride, trifluorochloroethylene, allylchloride, vinylidene chloride, vinylidene fluoride, diethyloroethylene, chlorocyclohexene, crotonaldehyde, acrylic aldehyde, cinnamic aldehyde, allyl alcohol, cyclohexenol, 4-methylpenten-3-ol-1, cinnamic alcohol; penten-4-ol-2, acrylic acid, methacrylic acid, crotonic acid, vinyl acetic acid, cinnamic acid, maleic acid, allylethyl ether, methyl acrylate, methyl methacrylate, vinylacetate, allylacetate, crotonamide, acrylamide, cinnamamide, acrylonitrile, methacrylonitrile, cinnamionitrile, vinyl dimethylamine, vinylmethyl sulphide, vinyl methyl ether, methylvinyl ketone, allyl acetone, perfluorovinyl methyl ether, allylisocyanate, ethylacrylate, 2-ethyl-hexylacrylate, n-butylacrylate, methylalpha-chloroacrylate, hydroxyethylacrylate, dihydroperfluorobutylacrylate, propylacrylate, isopropylacrylate, calcium acrylate, sodium acrylate, cyclohexylacrylate, dodecylacrylate, isobornylacrylate, hexyldecylacrylate, tetradecylacrylate, 2-n-tert-butylaminoethylmethacrylate, 2-butylmethacrylate, glycidylmethacrylate, 2-chloromethylmethacrylate, 3,3-dimethylbutylmethacrylate, 2-ethylhexylmethacrylate, 2-methoxyethylmethacrylate, pentylmethacrylate, ethylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, isopropylmethacrylate, propylmethacrylate, allylbenzoate, vinylbutyrate, vinylstearate, vinylbenzoate, dialkyl fumarates, dialkylmaleates, vinylidene bromide, vinyl naphthalene and vinyl pyridine.

The products prepared by the process described herein, will contain silyl groups in terminal positions. These products can be illustrated as to type by describing some of the reactions believed to take place in the silylating method of the present invention. In the following reactions, I is the initiator and C=C represents the organic vinylic monomer.

- (1) $I \cdot + C = C \rightarrow IC-C$
 (2) $IC-C \cdot - n(C = C) \rightarrow IC-C(C-C)_n$
 (3) $IC-C(C-C)_n \cdot + X_{3-x}R'_xSiRY \rightarrow IC-C(C-C)_nRSiR'_xX_{3-x} + Y$
 (4) $Y \cdot + (C = C) \rightarrow YC-C$
 5 (5) $YC-C + nC = C \rightarrow YC-C(C-C)_n$
 (6) $2YC-C(C-C)_n \cdot \rightarrow YC-C(C-C)_{2n}C-CY$

Therefore, the product will contain organic vinylic polymers having one silyl group at the end of each polymer chain. However, when



is used $\cdot SRSiR'_xX_{3-x}$ will replace Y in the above equations and the product will contain organic vinylic polymer chains with one terminal silyl group and organic vinylic polymer chains with two terminal silyl groups.

15 The products obtained from the process have hydrolyzable silicon functional groups and therefore further reactions or condensations through these groups provides the organic vinylic polymers with the ability to react at room temperature, to cure at room temperature, to chain extend at room temperature and therefore the thermoplastic organic vinylic polymers have an added dimension. For example, the thermoplastic organic vinylic polymers having silyl groups can be reacted with reactive silicone polymers such as hydroxyl terminated polydimethylsiloxane, hydroxylated organosiloxane resins to provide copolymers which can be used in making paints and coatings. The thermoplastic organic vinylic polymers having the silyl groups show adhesion to ceramics and metallic surfaces.

35 The following examples illustrate the present invention.

Example 1

An emulsion of 50.0 g. of styrene, 100 g. of water, 1.0 g. of sodium lauryl sulphate, 0.052 g. of potassium persulphate, 0.052 g. of sodium phosphate and 5.0 g.



was stirred under a nitrogen atmosphere at

70°C. for 2 hours and then at 95°C. for 2 hours. A portion of the resulting emulsified polymer was coagulated with $CaCl_2$ to give a cross-linked polymer which had 30 percent by weight extractables by using a continuous benzene extraction. The emulsified polymer contained 70 percent by weight of the polystyrene molecules with



terminal groups which cross-linked through the silicon-methoxy functionality. The water was removed from a 31 g. portion of the above emulsion polymer by evaporation to which had been added 0.05 g. of stannous octoate as the condensation catalyst. The resulting product was a hard, glassy cross-linked polymer which had only 20 percent by weight benzene extractable material. The polymer, therefore, contained 80 percent by weight of the polystyrene molecules with





terminal groups which cross-linked through the silicon-methoxy functionality. The chain transfer constant for



was 11.8×10^{-3} .

Example 2

Methyl methacrylate was polymerised in sealed ampoules at $79.5^\circ \pm 0.2^\circ C$. The polymerisation mixture was composed of 5 g. of methyl methacrylate, 8.2×10^{-3} g. of azobisisobutyronitrile and the silicon compound defined below in the amount indicated.

Silicon Compound	Chain Transfer Constant	Amount g.	Terminating Group of Polymethylmethacrylate
$(CH_3O)_3SiCH_2CH_2CH_2SH$	693×10^{-3}	0.001	$-SCH_2CH_2CH_2Si(OCH_3)_3$
$\{(CH_3O)_3SiCH_2CH_2CH_2S\}_2$	2.58×10^{-3}	0.15	$-SCH_2CH_2CH_2Si(OCH_3)_3$
$(CH_3O)_3Si$  CH_2Br	2.98×10^{-3}	0.15	$-CH_2$  $-Si(OCH_3)_3$

Example 3

Styrene was polymerised in sealed ampoules at $79.5^{\circ} \pm 0.2^{\circ}\text{C}$. The polymerisation mixture was composed of 5 g. of styrene; 7.9×10^{-3}

g. of azobisisobutyronitrile and the silicon compound defined below in the amount indicated.

Silicon Compound	Chain Transfer Constant	Amount g.	Terminating Group of polystyrene
$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$	5900×10^{-3}	7.85×10^{-3}	$-\text{SCH}_2\text{CH}_2\text{CH}_2\text{Si}-(\text{OCH}_3)_3$
$\{(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}\}_2$	11.8×10^{-3}	0.078	$-\text{SCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$

Example 4

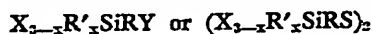
10 When the following silicon compounds having chain transfer constants greater than 10^{-3}

are substituted for the silicon compounds in Example 3, polystyrene is obtained having the indicated terminating groups.

Silicon Compound	Terminating Group
$\left[(\text{CH}_3\text{O})_3\text{Si} - \text{C}_6\text{H}_4 - \text{S} \right]_2$	$-\text{S} - \text{C}_6\text{H}_4 - \text{Si}(\text{OCH}_3)_3$
$\text{Cl}(\text{CH}_2)_2\text{SiCH}_2\text{SH}$	$\text{SCH}_2\text{Si}(\text{CH}_2)_2\text{Cl}$
O \parallel $(\text{CH}_2\text{CO})_2(\text{C}_6\text{H}_5)\text{SiC}_8\text{H}_{16}\text{SH}$	$-\text{SC}_8\text{H}_{16}\text{Si}(\text{C}_6\text{H}_5)(\text{OCCH}_3)_2$
$\left[\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \right]_3 \text{SiCH}_2\text{CH}_2\text{CH}_2\text{Br}$	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si} \left[\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \right]_3$

WHAT WE CLAIM IS:—

1. A method of preparing silyl-terminated organic vinylic polymers which comprises polymerising organic vinylic monomers by means of free radical initiation in the presence of an organosilicon compound of the formula



- 25 in which R' is a monovalent hydrocarbon radical free of aliphatic unsaturation and having from 1 to 18 carbon atoms, R is a divalent hydrocarbon radical free of aliphatic unsaturation and having from 1 to 18 carbon atoms, X is a monovalent hydrolysable radical as herein before defined, x is 0, 1 or 2 and Y is a free radical activated group having a chain transfer constant greater than 10^{-3} .

2. A method as claimed in claim 1 in which Y is a mercapto group or a bromine atom.

3. A method as claimed in claim 1 or claim 2 in which X is a methoxy group, R is propylene or $-\text{C}_6\text{H}_4\text{CH}_2-$ and x is 0.

4. A method as claimed in claim 1 in which the organosilicon compound is



5. A method as claimed in claim 1 substantially as described with reference to any of the Examples.

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